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(54) Title: DEGRADABLE COPOLYMERS FOR CHEWING GUM BASE

(57) Abstract: Improved degradable gum bases comprising condensation copolymers are disclosed which are polymerized from a first monomer which is capable of polymerization by condensation polymerization, e.g., ring opening lactone polymerization, and a second monomer which is effective to suppress the crystallization of the copolymer. It is disclosed that the copolymers can provide enhanced properties in degradable gum bases made from the copolymers.

DEGRADABLE COPOLYMERS FOR CHEWING GUM BASE

FIELD OF THE INVENTION

The present invention generally pertains to the use of degradable copolymers such as polycaprolactone copolymers in chewing gum base and more particularly to degradable condensation copolymers for use in chewing gum base.

BACKGROUND ON THE INVENTION

The art of chewing gum manufacture is well established. Gum formulations typically comprise a gum base comprising one or more polymers, e.g., natural or synthetic elastomers or thermoplastic polymers, as well as other common ingredients such as fillers, softeners and pigments. In addition, gum formulations typically contain flavorants, sweeteners and the like.

Conventional chewing gums adhere strongly to a variety of surfaces including, for example, wood floors, asphalt pavement, concrete, carpet, leather, hair, and cloth. Discarded chewing gums that are stuck to those surfaces are often difficult and costly to remove. Moreover, such inappropriately discarded chewing gums can be environmentally obnoxious and aesthetically displeasing. Oftentimes, even after the chewing gums have been removed, stains are left on the surfaces. As a result, in some locations, vendors have been banned from selling chewing gums to consumers in many public places such as train stations, arenas, amusement parks, and schools. Accordingly, a chewing gum that is degradable or easily removable from the surfaces on which it is discarded or deposited would be highly desirable.

One polymer commonly used in gum bases is polyvinyl acetate. Polyvinyl acetate is a very desirable component in chewing gum because it has the following characteristics: it is an amorphous polymer which; swells in water, retains solidity, controls flavor release, is compatible with polar sugars and flavors, softens at body temperature, is cohesive, is non-toxic and does not adhere to dental work. However, the degradability of polyvinyl acetate is somewhat limited.

Polycaprolactone is a known degradable polymer which has been proposed for use in gum bases. For example, U.S. Patent No. 5,672,367 discloses the use of polyesters, e.g., polycaprolactone, based on the polymerization product of one or more cyclic esters. However, as compared to polyvinylacetate, polycaprolactone does not swell readily in water and is a semi-crystalline polymer. Polycaprolactone has a melting point of 60°C, whereas body temperature is approximately 40°C. In order for polycaprolactone to be useful in chewing gum and be commercially acceptable, the softening point would need to be reduced, preferably to body temperature or below. In addition, the polymer should swell in water or absorb water. Otherwise, the hard crystalline portion of the polymer could lead to undesirable chew characteristics in the mouth.

Accordingly, improved degradable polymers suitable for use in gum bases are desired.

SUMMARY OF THE INVENTION

By the present invention, improved gum bases comprising degradable condensation copolymers are provided. The improvement of the present invention is directed to the use of comonomers in the condensation polymerization which are effective to suppress the

crystallinity of the copolymers. Without being bound to any particular theory, it is believed that the suppression of crystallinity can cause enhancements in the properties of gum bases made from the copolymers of the present invention compared to copolymers made without the crystallinity-suppressing monomers.

As used herein, the terms "condensation polymerization" and "polycondensation" mean: (i) a polymerization reaction in which two or more molecules are combined with the generation of water, alcohol or other simple substances as by-products; and (ii) polymerization of monomers, e.g., ester and amide monomers, formed by ring opening polymerization, e.g., lactones, lactides and lactams, which do not generate water, alcohol or other simple substances as by-products.

In accordance with the present invention, the suppression of crystallinity may be evidenced by one or more factors. For instance, the suppression of crystallinity may be evidenced by a reduction in the crystallization temperature of the copolymer, or by a reduction in the rate of crystallization of the copolymer, or by a reduction in the melt temperature of the copolymer, or by a reduction in the crystallinity of the copolymer or by a reduction in the Vicat softening point of the copolymer. As used herein, the term "crystallization temperature" means the temperature at which formation of the crystalline phase occurs; the term "crystallization rate" means the rate at which formation of the crystalline phase occurs; the term "melt temperature" means the freezing point and the term "crystallinity" means the degree of crystallinity of the polymer. The crystallization properties of polymers can be readily determined by those skilled in the art, such as, for example, by differential scanning calorimetry ("DSC").

The present invention also provides degradable polymers for use in gum base which do not stick readily to indoor or outdoor surfaces. Degraded polymers are more easily removable from typical substrates.

Gum bases containing the degradable polymers of the present invention after being chewed, can become brittle, easily break up and adhere less to indoor and outdoor surfaces.

DETAILED DESCRIPTION OF THE INVENTION

Apart from the degradable copolymers of the present invention, the composition of the gum base is not critical to the present invention. The composition of the gum bases of the present invention can vary depending upon factors known in the art such as, for example, the type of base desired, e.g., bubble gum, the consistency of gum desired, e.g., hard or soft, and the other components used in the composition to make the final chewing gum product. Illustrative examples of suitable polymers in gum bases include both natural and synthetic elastomers and rubbers such as, for example, elastomers of vegetable origin such as chicle, natural rubber, crown gum, nispero, rosidinha, jelutong, perillo, niger gutta, tunu, balata, guttapercha, lechi capsi, sorva, gutta kay, mixtures thereof, and the like, and synthetic elastomers such as butadiene-styrene copolymers, polyisobutylene, isobutylene-isoprene copolymers, polyethylene, mixtures thereof, and the like.

Suitable gum bases may also include a synthetic thermoplastic polymer, such as, for example, polyvinyl acetate and its partial hydrolysate, ethylene vinyl acetate, polyvinyl alcohol, and mixtures thereof and the like. When utilized, the molecular weight of the thermoplastic polymer typically is in the range of from about 2,000 to about 100,000 grams per gram mole ("g/gmol"). Unless otherwise indicated, as used herein, the term "molecular weight" means number average molecular weight. Techniques for determining number average molecular weight are known to those skilled in the art. One such technique is gel permeation chromatography ("GPC").

The gum base may also include plasticizers or softeners such as, for example, lanolin, palmitic acid, oleic acid, stearic acid, sodium stearate, potassium stearate, glyceryl triacetate, glyceryl lecithin, glyceryl monostearate, propylene glycol monostearate, acetylated monoglyceride, glycerine, triethylcitrate, epoxidized soybean oil, epoxidized linseed oil, acetyltriethyl citrate, tri-n-butyl citrate, acetyltri-n-butyl citrate, acetyltri-n-hexyl citrate, mixtures thereof, and the like. Natural and synthetic waxes, hydrogenated vegetable oils, organic waxes such as polyurethane waxes, polyethylene waxes, paraffin waxes, microcrystalline waxes, fatty waxes, sorbitan monostearate, tallow, polypropylene glycol, mixtures thereof, and the like, may also be incorporated into the gum base. Such materials are typically incorporated into the gum base to provide a variety of desirable textures and consistency properties. The low molecular weight of these ingredients, (relative to the molecular weight of the polymers) enable them to penetrate the gum base making it plastic and less viscous. Alternatively, plasticizers can be incorporated, such as through extrusion or melt mixing, into the polymer component of the gum base prior to mixing with the other gum base ingredients. These additional materials are generally employed in amounts up to about 18%, preferably in amounts from about 5% to about 18%, and more preferably in amounts from about 10% to about 14%, by weight of the gum base.

The gum base may also include mineral adjuvants such as, for example, calcium carbonate, magnesium carbonate, alumina, aluminum hydroxide, aluminum silicate, talc, tricalcium phosphate, dicalcium phosphate and the like, as well as mixtures thereof. These mineral adjuvants typically serve as fillers and textural agents. These fillers or adjuvants may be used in the gum base in various amounts.

Preferably, the amount of adjuvants, when used, will be present in an amount up to about 60%, by weight of the chewing gum base.

Other traditional ingredients which may be used in the gum base include, for example, coloring agents, antioxidants, preservatives, and the like. Typically, coloring agents are used in gum formulations to produce the desired color. These coloring agents include pigments which may be incorporated, for example, in amounts up to about 6%, by weight of the gum composition. A preferred pigment, titanium dioxide, is typically incorporated in amounts up to about 2%, and preferably less than about 1%, by weight of the gum formulation. The colorants may also include natural food colors and dyes suitable for food, drug and cosmetic applications. These colorants are known as F.D.&C. dyes and lakes. The materials acceptable for the foregoing uses are preferably water-soluble. A recitation of F.D.&C. colorants and their corresponding chemical structures may be found in the Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, in volume 5 at pages 857-885. An anti-oxidant such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), propyl gallate, and mixtures thereof, may also be included.

The amount of gum base employed in the gum formulation will also vary depending upon factors known to those skilled in the art such as, for example, the type of base used, the consistency of the gum desired and the other components used in the composition to make the final chewing gum product. In general, the gum base will typically be present in amounts from about 5% to about 50%, preferably in amounts from about 15% to about 40%, and more preferably in amounts from about 23% to about 35%, by weight of the final chewing gum formulation.

The chewing gum formulations containing the gum base usually include flavoring agents and sweetening agents as well as other

conventional ingredients such as described above with respect to the gum bases, including, for example, plasticizers, softeners, emulsifiers, waxes, fillers, bulking agents, mineral adjuvants, coloring agents, antioxidants, acidulants, thickeners, mixtures thereof, and the like. Further specific examples include emulsifiers, such as lecithin and glyceryl monostearate, thickeners, used alone or in combination with other softeners, such as, for example, methyl cellulose, alginates, carrageenan, xanthan gum, gelatin, carob, tragacanth, locust bean, and carboxy methyl cellulose, acidulants such as maleic acid, adipic acid, citric acid, tartaric acid, fumaric acid, and mixtures thereof. Some of these additives may serve more than one purpose. For example, in sugarless gum compositions, a sweetener, such as sorbitol or other sugar alcohol or mixtures thereof, may also function as a bulking agent.

Typical flavoring agents which may be used include those natural and synthetic flavors known to those skilled in the art. These flavorings may be chosen, for example, from synthetic flavor oils and flavoring aromatics or oils, oleoresins and extracts derived from plants, leaves, flowers, fruits, and so forth, and combinations thereof. Nonlimiting representative flavor oils include, for example, spearmint oil, cinnamon oil, oil of wintergreen (methyl salicylate), peppermint oil, clove oil, bay oil, anise oil, eucalyptus oil, thyme oil, cedar leaf oil, oil of nutmeg, allspice, oil of sage, mace, oil of bitter almonds, and cassia oil. Also, useful flavorings are artificial, natural and synthetic fruit flavors such as vanilla, and citrus oils including lemon, orange, lime, grapefruit, and fruit essences including apple, pear, peach, grape, strawberry, raspberry, cherry, plum, pineapple, apricot and so forth. These flavoring agents may be used in liquid or solid form and may be used individually or in admixture. Commonly used flavors include, for example, mints such as peppermint, menthol, artificial vanilla,

cinnamon derivatives, and various fruit flavors, whether employed individually or in admixture.

Other useful flavorings include, for example, aldehydes and esters such as cinnamyl acetate, cinnamaldehyde, citral diethylacetal, dihydrocarvyl acetate, eugenyl formate, p-methylamisol, and the like. Generally, any flavoring or food additive such as those described in Chemicals Used in Food Processing, publication 1274, pages 63-258, by the National Academy of Sciences, may be used.

Suitable apparatus useful in accordance with the present invention for manufacture of the chewing gum comprise mixing and heating apparatus known in the chewing gum manufacturing arts. Therefore the selection of the specific apparatus will be apparent to those skilled in the art.

Typically, processes for making gum formulations involve the following steps. First, a gum base is heated to a temperature sufficiently high to soften the base without adversely affecting the physical and chemical make up of the base. The temperatures utilized may vary depending upon the composition of the gum base used, but such temperatures are readily determined by those skilled in the art without undue experimentation. The gum base is conventionally melted at temperatures that range from about 60° C to about 120° C for a period of time sufficient to render the base molten. For example, the gum base may be heated under those conditions for a period of about thirty minutes just prior to being admixed incrementally with the remaining ingredients of the gum such as plasticizers, softeners, bulking agents, sweeteners, and/or fillers, coloring agents and flavoring agents to plasticize the blend as well as to modulate the hardness, viscoelasticity and formability of the base. Mixing is continued until a uniform mixture of gum formulation is obtained.

Thereafter, the gum formulation may be further processed as known in the art. For instance, in the preparation of confectionery coated chewing gum compositions, the gum formulation is formed into portions which are then placed in a revolving coating pan. A confectionery coating syrup is prepared, heated if necessary, and then applied to the gum portions. The coated gum portions are then allowed to cool and dry. Various additional ingredients will usually be incorporated into the confectionery coating composition as dictated by the nature of the desired composition as well known by those skilled in the art.

The gum formulations containing the degradable copolymers of the present invention may be used to provide a variety of chewing gum product formats, such as sticks, slabs, chunks, balls, ropes, tablets, and center filled and confectionery coated gum products. Examples of suitable gum formulations may be found for example in U.S. Pat. Nos. 4,961,935; 4,514,422; 4,382,963; 4,579,738; 5,498,429 and 5,601,858. Further details of gum formulations are known to those skilled in the art.

The degradable copolymers suitable for use in the gum bases of the present invention are polymerized from a first and second monomer.

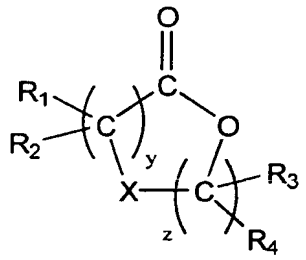
The first monomer suitable for use in accordance with the present invention can be any monomer which is polymerizable by condensation polymerization. The first monomer can be ethylenically unsaturated or alternatively can have no ethylenic unsaturation. The molecular structure of the first monomer is not critical for the present invention and can be linear, e.g., normal, alkyl or branched, cyclic or aromatic. Preferably, the first monomer has functional groups selected from the group consisting of esters, ethers, alcohols, acids, amines, amides, acid halides, isocyanates and mixtures thereof as may be

determined by those skilled in the art. In addition, the first monomer can be comprised of a single molecular unit, an oligomer or a prepolymer and can have a molecular weight of typically from about 62 to 12,000 g/gmol, more typically, from about 62 to 10,000 g/gmol.

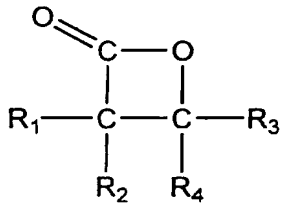
In one aspect of the present invention, the first monomer comprises one or more compounds which can be polymerized or copolymerized to form aliphatic polyesters or polyester amides or other condensation polymers. Examples of such polymers include, for example, polyesters prepared from the reaction of C_2-C_6 diols, e.g., ethylene glycol, diethylene glycol, butanediol, neopentyl glycol, hexanediol with dicarboxylic acids, such as but not limited to, succinic, glutaric or adipic acid; copolyesters of terephthalic acid based polymers with dicarboxylic acids and diols; and polyester/amides from the reaction of caprolactam with dicarboxylic acids and diols. Suitable hydroxy acids include, for example, α-hydroxybutyric acid, α-hydroxyisobutyric acid, α-hydroxyvaleric acid, α-hydroxyisovaleric acid, α-hydroxycaproic acid, α-hydroxyisocaproic acid, α-hydroxy-α-ethylbutyric acid, α-hydroxy-β-methylvaleric acid, α-hydroxyheptanoic acid, α-hydroxyoctanoic acid, α-hydroxydecanoic acid, α-hydroxymyristic acid and α-hydroxystearic acid or their intermolecular cyclic esters or combinations thereof.

In another aspect of the present invention, the first monomer comprises cyclic monomers which are polymerized by ring opening polymerization. Typical of such monomers are cyclic esters, such as, for example, lactides, glycolides, lactones and cyclic carbonates.

In one aspect of the present invention, the cyclic monomers include those having the formulas:



where X=nil, -O-, or -O-C=O; Z=1-3; Y=1-4; R_1-R_4= H-, -CH_3, C_2-C_{16} alkyl group, -C(CH_3), or $HOCH_2$-, and where all R's are independent on each y or z carbon unit and independent of each other; or

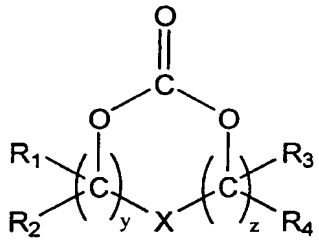


where R_1-R_4= H-, -CH_3, C_2-C_{16} alkyl group, or $HOCH_2$-, and where all R's are independent of each other.

Examples of the lactones described above are, but not limited to, ε-caprolactone, t-butyl caprolactone, zeta-enantholactone, deltavalerolactones, the monoalkyl-delta-valerolactones, e.g. the monomethyl-, monoethyl-, monohexyl-deltavalerolactones, and the like; the nonalkyl, dialkyl, and trialkyl-epsilon-caprolactones, e.g. the monomethyl-, monoethyl-, monohexyl-, dimethyl-, di-n-propyl-, di-n-hexyl-, trimethyl-, triethyl-, tri-n-epsilon-caprolactones, 5-nonyl-oxepan-2-one, 4,4,6- or 4,6,6-trimethyl-oxepan-2-one, 5-hydroxymethyl-oxepan-2-one, and the like; beta-lactones, e.g., beta-propiolactone, beta-butyrolactone gamma-lactones, e.g., gammabutyrolactone or pivalolactone, dilactones, e.g. lactide, dilactides, glycolides, e.g.,

tetramethyl glycolides, and the like, ketodioxanones, e.g. 1,4-dioxan-2-one, 1,5-dioxepan-2-one, and the like. The lactones can consist of the optically pure isomers or two or more optically different isomers or can consist of mixtures of isomers.

In addition cyclic carbonates of the formula:



where X=nil,-O-; Z=1-3; Y=1-3; R_1-R_4= H-, -CH_3, C_2-C_{16} alkyl group, or $HOCH_2$-, and where all R's are independent on each y or z carbon unit and independent of each other, can be used as a comonomer with the lactones of this invention.

Examples of suitable cyclic carbonates are ethylene carbonate, 3-ethyl-3-hydroxymethyl trimethylene carbonate, propylene carbonate, trimethylene carbonate, trimethylolpropane monocarbonate, 4,6-dimethyl-1,3-propylene carbonate, 2,2-dimethyl trimethylene carbonate, and 1,3-dioxepan-2-one.

ε-caprolactone and its derivatives and other seven membered ring lactones are especially preferred for use as first monomers in accordance with the present invention.

Examples of typical cyclic ester polymers and their copolymers resulting from the polymerization of the above-mentioned monomers include, but are not limited to: poly(L-lactide); poly(D-lactide); poly(D,L-lactide); poly(mesolactide); poly(glycolide); poly(trimethylenecarbonate); poly(epsilon-caprolactone); poly(L-

lactide-co-D,L-lactide); poly(L-lactide-co-meso-lactide); poly(L-lactide-co-glycolide); poly(L-lactide-co-trimethylenecarbonate); poly(L-lactide-co-epsilon-caprolactone); poly(D,L-lactide-co-meso-lactide); poly(D,L-lactide-co-glycolide); poly(D,L-lactide-co-trimethylenecarbonate); poly(D,L-lactide-co-epsilon-caprolactone); poly(meso-lactide-co-glycolide); poly(meso-lactide-co-trimethylenecarbonate); poly(meso-lactide-co-epsilon-caprolactone); poly(glycolide-co-trimethylenecarbonate); poly(glycolide-co-epsilon-caprolactone).

Typically, the amount of the first monomer used in the copolymers of the present invention is from about 51 to 99.1 wt. %, preferably from about 51 to 75 wt. % and more preferably from about 55 to 70 wt. %, based on the total weight of the monomers in the copolymer. Monomers suitable for use as the first monomer in the copolymers of the present invention are commercially available.

The second monomer suitable for use in preparing the copolymers of the present invention includes any monomers which are functional to suppress the crystallinity of the copolymer or any monomers which are functional to decrease the surface tension or coefficient of friction of the copolymer. The second monomer can be ethylenically unsaturated or alternatively can have no ethylenic unsaturation. The molecular structure of the second monomer is not critical for the present invention and can be straight, e.g., normal, alkyl or branched, cyclic, or aromatic. In a preferred aspect of the invention, the second monomer is a semi-crystalline lactide or an amorphous ester. Preferably, the second monomer has a functional group selected from the group consisting of esters, ethers, alcohols, acids, amides, acid halides, siloxanes, silanols, and mixtures thereof. In addition, the second monomer can be comprised of a single molecular unit, an oligomer or a prepolymer and can have a molecular weight of typically from about 50 to 20,000 g/gmol, more typically,

from about 50 to 16,000 g/gmol. Additionally, the second monomer can comprise a derivative of the first monomer, e.g, a branched caprolactone such as, for example, t-butyl caprolactone.

Often, the second monomer is used as an initiator in the polymerization of the first monomer, e.g., to initiate ring opening of cyclic lactone monomers. Typically, the suppression in crystallinity afforded by the second monomer for use in a gum application will be evidenced by one or more of the following factors: (i) a reduction in the melting point of the copolymer of at least 2°C, preferably at least 3°C and more preferably at least 7°C, as compared to a homopolymer of the first monomer or a copolymer of the first monomer and another monomer which is not effective to suppress the crystallinity, or (ii) a reduction in the crystallization temperature of the copolymer of at least 2°C, preferably at least 3°C and more preferably at least 7°C, as compared to a homopolymer of the first monomer or a copolymer of the first monomer and another monomer which is not effective to suppress the crystallinity, (iii) a reduction in the Vicat softening point of the copolymer of at least 2°C, preferably at least 3°C and more preferably at least 7°C, as compared to a homopolymer of the first monomer or a copolymer of the first monomer and another monomer which is not effective to suppress the crystallinity or (iv) a reduction in the crystallinity of the copolymer. Typically, in accordance with the present invention, the crystallinity will be reduced by at least 2 percent, preferably at least 6 percent and more preferably at least 8 percent compared to the crystallinity of a homopolymer of the first monomer or a copolymer of the first monomer and another monomer which is not effective to suppress the crystallinity. The crystallinity can be determined by DSC, measuring the enthalpy of fusion.

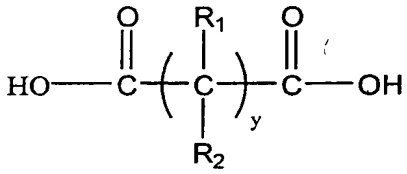
In one aspect of the present invention, the second monomer is effective to create amorphous regions in the copolymer. For example if the second monomer is a branched version of the first monomer, it generally will not co-crystallize with the first monomer, thus it will disrupt the crystallization of the first monomer, increasing the amorphous region, decreasing the crystallinity of the copolymer. If the second 'monomer' is a non-crystallizable oligomer, the net crystallinity of the copolymer will be reduced.

In another aspect of this invention, the second monomer is effective to improve the water uptake, i.e., the amount of water absorbed by the copolymer after 24 hours at 40° C. Preferably, the water uptake is at least 5% greater, more preferably at least 10% greater than the water uptake of a homopolymer of the first monomer.

In another aspect of this invention, the second monomer is effective to produce a polymer which when formulated into a gum formulation and after being chewed and expelled to a surface, has less adhesion to that surface and/or becomes brittle after a short period of time. Preferably, the copolymer is effective to enhance the removability of the gum base from surfaces upon which the gum base is deposited after chewing.

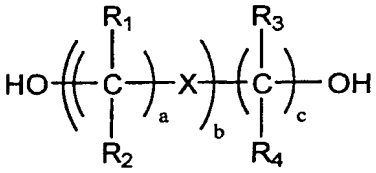
In one aspect of the invention, the second monomer can be an ester formed by polymerizing a linear or branched dicarboxylic acid with a linear or branched diol.

Suitable dicarboxylic acids are of the formula:



where Y=0 to 12; R_1 and R_2 = H-, -CH_3 or C_2-C_{16} alkyl group, and where all R's are independent of each other and each carbon unit. Illustrative of the dicarboxylic acids are succinic acid, glutaric acid, adipic acid, suberic acid, sebacic acid, dodecanedioic acid, and 2-ethyl-2-methylsuccinic acid. In addition to the aliphatic dicarboxylic acids described above, aromatic dicarboxylic acids, such a, but not limited to, phthalic acid, isophthalic acid, and terephthalic acid can be used.

Suitable diol initiators are of the formula:



where X= nil, -O-; a=1 to 6; b=0 to 10; c=nil, C_1-C_{16}; and R_1-R_4= H-, -CH_3 or C_2-C_{16} alkyl group, and where all R's are independent of each other and each carbon unit. Examples of diols are, but not limited to, ethylene glycol, diethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol, 1,12-dodecanediol, 1,2-decanediol, 1,2-dodecanediol, 1,2-hexadecanediol, neopentyl glycol, 3-methyl-1,5-pentanediol, 2-methyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-ethyl-3-butyl-1,3-propanediol, 2-ethyl-1,6-hexanediol.

The amount of the second monomer suitable for use in preparing the copolymers of the present invention is effective to suppress the crystallinity of the copolymer. Typically, the amount is from about 0.1 to 40 wt. %, preferably from about 25 to 40 wt. % and more preferably from about 30 to 45 wt. % based on the total weight of the monomers used to make the copolymer. The optimal level of the second monomer will depend of the specific structure of the second monomer and can be determined by those skilled in the art.

One or more monomers from each of the first monomer group or second monomer group may be used in preparing the copolymers of the present invention.

In addition to other monomers, the copolymers of the present invention may be blended and/or reacted with other polymers to provide desired characteristics. For instance, the copolymers of the present invention may be extruded with other polymers, such as, for example, polyvinyl acetate, polysaccharides, e.g., , starch, cellulosics, chitans and the like. Further details of such blended polymer compositions are known to those skilled in art. See for example, U.S. Patent No. 5,095,054 which is directed to thermoplastic polymer compositions comprising destructurized starch and other polymers, U.S. Patent No. 5,540,929 which is directed to aliphatic polyester grafted polysaccharides.

Typically, when the copolymers of the present invention are blended or reacted with other polymers, the amount of the other polymer is typically from about 0 to 70 wt. % and preferably from about 20 to 60 wt. % and more preferably from about 30 to 50 wt. % based on the total weight of the blended polymer composition.

Another aspect of the present invention is directed to the production of star polymers. In this aspect of the invention, star polymers can decrease the crystallinity of the homopolymer. Examples of star polymers are, but not limited to, polymers of monomer 1, such as ε-caprolactone, with multifunctional initiators such as trimethylolpropane, pentaerythritol, dipentaerythritol and other molecules with multiple hydroxyl or other reactive groups.

The gum bases of the present invention typically comprise from about 1 to 99 wt%, preferably from about 10 to 90 wt% and more preferably from about 20 to 80 wt% of the copolymers of the present invention.

The processes used to prepare the copolymers of the present invention are not critical. The polymer of the present invention can be prepared by bulk polymerization, suspension polymerization, extruder or solution polymerization. The polymerization can be carried out, for example, in the presence of an inert normally-liquid organic vehicle such as, for example, aromatic hydrocarbons, e.g., benzene, toluene, xylene, ethylbenzene and the like; oxygenated organic compounds such as anisole, dimethyl, and diethyl esters of ethylene glycol; normally-liquid hydrocarbons including open chain, cyclic and alkyl-substituted cyclic saturated hydrocarbons such as hexane, heptane, cyclohexane, decahydronapthalene and the like.

The polymerization process can be conducted in a batch, semi-continuous, or continuous manner. The monomers and catalysts can be admixed in any order according to known polymerization techniques. Thus, the catalyst can be added to one comonomeric reactant. Thereafter, the catalyst-containing comonomer can be admixed with another comonomer. In the alternative, comonomeric reactants can be admixed with each other. The catalyst can then be added to the reactant mixture. If desired, the catalyst can be dissolved or suspended in an inert normally-liquid organic vehicle. If desired, the monomeric reactants either as a solution or a suspension in an inert organic vehicle can be added to the catalyst, catalyst solution or catalyst suspension. Still further, the catalyst and comonomeric reactants can be added to a reaction vessel simultaneously. The reaction vessel can be equipped with a conventional heat exchanger and/or mixing device. The reaction vessel can be any equipment normally employed in the art of making polymers. One suitable vessel, for example, is a stainless steel vessel. A plasticizer, if used, or a solvent can be blended into the polymer to aid in removal of the polymer material from the reactor vessel.

Typically, the polymerization reactions are conducted at a temperature of from about 70 to 250°C, preferably from about 100 to 220°C, over a reaction time of from about 3 minutes to 24 hours preferably from about 5 to 10 hours. The reaction pressure is not critical to the present invention. The particular catalyst used in the polymerization is not critical and can be determined by those skilled in the art. However, one preferred catalyst for the polymerization of caprolactone with lactides or diols is tin carboxylate. The catalyst and initiator may be combined in the same molecule, e.g., an aluminum alkoxide.

The copolymers produced in accordance with the present invention typically have a melting point of from about 20 to 55°C, preferably from about 30 to 50°C, and a Tg of from about -120 to 120°C and preferably from about -60 to 60°C.

Typically, the copolymers of the present invention have a weight average molecular weight (Mw) of from about 500 to 300,000 grams/gram mole, and preferably from about 10,000 to 225,000 grams/gram mole. Typically, the number average molecular weight (Mn) ranges from about 500 to 100,000 grams/gram mole, preferably from about 10,000 to 90,000 grams/gram mole. The Polydispersity Index (M_w/M_n) typically ranges from about 1.3 to 10.

Upon completion of the polymerization reaction, the copolymers can be recovered by any means known to those skilled in the art. Preferably in accordance with the present invention, the copolymer is transported in its molten state directly to a pelletizer, extruder or molding machine in order to produce the desired product.

Typically the copolymers of the present invention are substantially biodegradable. More specifically, the copolymer compositions typically are biodegradable and compostable by ASTM D-

5338, which is a standard test method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions.

Examples

The following Examples are provided for illustrative purposes and are not intended to limit the scope of the claims which follow.

The following test procedures were used in the Examples.

GPC Test Procedure

GPC was conducted on a Waters 590 HPLC unit having a LC-241 Autosampler, Waters Styragel columns HR-1, HR-3, HR-4, HR-4E, HR-5E, a ERMA ERC-7510 Differential Refractometer Detector connected to a VG Data System, using tetrahydrofuran (stabilized with BHT) as the solvent, 0.45u PTFE disposable filters (for sample preparation) and a 0.45u Nylon 66 filter (for mobile phase degassing). The unit was calibrated using polystyrene standards in the molecular weight range of 162 to 1,800,000. The operating parameters were:

Flow	1.0ml/min.
Run Time	65 minutes
Injection Size	200 ul
Temperatures	
Detector	35c
Columns	Ambient
Injector	Ambient

The sample concentration was 0.5 percent weight/volume.

Differential Scanning Calorimetry (DSC)

DSC for polymers were measured in a helium atmosphere from -100°C to 200°C at a rate of 10°C/minute. The effect of crystalline suppression by addition of the second monomer was determined using

DSC. The effect is shown with a depression of the temperature of crystallization (Tc), and on second heat depression of the melting point (Tm2) and a decrease in crystallinity as measured by a reduction in the heat of fusion (ΔH_f).

Vicat Softening Point

Polymers were pressed into plaques of approximately 120 mil thick. The Vicat Softening point was measured on the samples according to ASTM Method D-1525 utilizing Rate A, 50°C per hour. The softening temperature was recorded as the temperature at which a flat-tipped needle of 1-mm^2 circular cross section has penetrated the sample to a depth of 1mm under a load of 1000 grams.

Water Swell

Polymers were pressed into plaques of approximately 25-35 mils thick. The samples were dried in a 40°C oven for 24 hours and then weighed. They were then submerged into water and placed in an oven at 40°C oven for 24 hours and then reweighed. The difference in weight is then determined and divided by the initial weight and the % water uptake is recorded.

Biodegradability

ASTM D-5338, which is a standard test method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, was used to determine the biodegradability of copolymer.

Ease of Removability From Surfaces

Several known polymer test methods were utilized to determine differences in surface tension, adhesion and/or ease of removability from various surfaces. A modified method of the ASTM D1876 peel resistance for adhesives was used on cement and metal substrates. Surface tension was determined utilizing ASTM method D2578. Tack testing and abrasion testing were also performed on the polymers disclosed in this invention. Coefficient of friction was determined on thin plaques of the polymers disclosed in this invention following ASTM procedure.

The following ingredients were used in the Examples.

TONE® Monomer ECEQ - a ε-caprolactone monomer available from Union Carbide Corporation, Danbury, CT.

TONE® Polymer P-737 - a polymer of 32,000 Mn available from Union Carbide Corporation, Danbury, CT.

TONE® Polymer P-767 - a polymer of 50,000 Mn available from Union Carbide Corporation, Danbury, CT.

Polybutadiene, hydroxyl functionalized - 3080 Mn by GPC analysis from Aldrich.

Carbowax PEG 4000 - a polymer of 4000 Mn available from Union Carbide Corporation, Danbury, CT.

EXAMPLES 1-3

PREPARATION OF CAPROLACTONE POLYMERS

Caprolactone polymers were prepared, with GPC molecular weights >15,000, in a 4-neck resin kettle equipped with an agitator, nitrogen sparge tube and flow meter, a thermocouple connected to a temperature controlled oil bath, and vacuum. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and diethylene glycol. To remove moisture from the

reaction the reactants are dried in a nitrogen environment at 80°C under vacuum. After the residual water was reduced to <100 ppm the vacuum was discontinued and the temperature was raised to 120°C, charged with a suitable amount of a metal carboxylate catalyst, and then the temperature was increased to obtain a material temperature >140°C. The reaction was held at temperature until the % residual ε-caprolactone monomer was <1%. The polymers were discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 4

PREPARATION OF STAR-BRANCHED CAPROLACTONE POLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare a pentaerythritol initiated caprolactone polymer. The polymer was discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 5

PREPARATION OF POLYBUTADIENE CAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare a caprolactone copolymer initiated from hydroxyl functionalized polybutadiene of GPC Mn 3080. The polymer was discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 6

PREPARATION OF BDO ADIPATE MONOMER

1,4-Butanediol ("BDO") adipate monomer was prepared in a 4-neck resin kettle equipped with a condenser and dean stark trap, agitator, nitrogen sparge tube and flow meter, and a thermocouple connected to a temperature controlled heating mantle. On a mole basis, the reactor was charged with the proper amount of BDO, adipic acid, and 10% toluene by weight as an azeotrope solvent. The azeotrope solvent is included to remove water produced as a byproduct of the reaction. The reaction was conducted under nitrogen and heated to 140°C. After water stopped collecting in the Dean Stark trap, the temperature was raised in 20°C increments to 220°C and held until >95% of the theoretical amount of water to be removed was obtained. The temperature was lowered to 160°C, a suitable amount of a metal carboxylate catalyst was charged, the temperature was raised to a maximum of 220°C, and the reaction allowed to continue for 12 to 16 hours until the acid number was <10. A BDO adipate having an acid number of 8.9 and GPC molecular weights of Mn 12000, Mw 38395, Mw/Mn 3.20 was obtained.

EXAMPLE 7

PREPARATION OF LINEAR BDO ADIPATE CAPROLACTONE COPOLYMER

A procedure substantially similar to that described in Example 1 was used to prepare a caprolactone/butanediol adipate copolymer. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and butanediol adipate monomer from Example 6. The polymer was discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 8

PREPARATION OF BEPD ADIPATE MONOMERS

2-Butyl-2-ethyl-1,3-propanediol ("BEPD") adipates in the molecular weight range of 4000 to 21000, as determined by GPC, were prepared in a procedure substantially similar to that described in Example 6, except that the reaction was continued until the acid number was < 4. The acid number and GPC molecular weight of the product were determined.

EXAMPLES 9 - 11
PREPARATION OF BEPD ADIPATE CAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare a caprolactone/BEPD adipate copolymer. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and BEPD adipate monomer from Example 8. Alternately, star polymers can also be included by addition of 20 to 120 ppm trimethylolpropane. The polymers were discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 12
PREPARATION OF MIXED DIOL ADIPATE MONOMERS

Mixed diol adipates in the molecular weight range of 4000 to 21000, as determined by GPC, were prepared in a procedure substantially similar to that described in Example 6. For purposes of illustration, adipates from ethylene glycol (EG) and BEPD, and neopentyl glycol (NPG) and BEPD were made. The acid number and GPC molecular weight of the product were determined.

EXAMPLES 13-15
MIXED DIOL ADIPATE POLYCAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare caprolactone/BEPD/NPG adipate copolymers and caprolactone/BEPD/EG adipate copolymers. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and BEPD/EG adipate or BEPD/NPG adipate monomer from Example 12. The polymers were discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 16
ADDITION OF LACTIDE TO BRANCHED BEPD ADIPATE MONOMER

BEPD Adipate/Lactide copolymers were prepared, with GPC molecular weights >5,000, in a 4-neck resin kettle equipped with an agitator, nitrogen sparge tube and flow meter, a thermocouple connected to a temperature controlled oil bath, and vacuum. On a mole basis, the reactor was charged with the proper amount of L-Lactide monomer and BEPD Adipate monomer from Example 8. To remove moisture from the reaction the reactants are dried in a nitrogen environment at 80°C under vacuum. After the residual water was reduced to <100 ppm the vacuum was discontinued and the temperature was raised to 120°C, charged with a suitable amount of a metal carboxylate catalyst, and then the temperature was increased to obtain a material temperature >140°C. The reaction was held at temperature until the % residual L-lactide monomer was <2%. The hydroxyl number, acid number, GPC molecular weight, and composition by NMR of the product were determined.

EXAMPLES 17 & 18

PREPARATION OF BEPD ADIPATE LACTIDE CAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare caprolactone/BEPD adipate lactide copolymers. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and BEPD adipate lactide monomer from Example 16. The polymers were discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 19

PREPARATION OF DEG LACTIDE POLYOL MONOMER

A procedure substantially similar to that described in Example 1 was used to prepare lactide polyols intiated from diethylene glycol initiator (DEG) with GPC molecular weights <20,000. The reaction was held at temperature until the % residual L-lactide monomer was <2%. The GPC molecular weight and composition by NMR of the product were determined.

EXAMPLES 20-29

PREPARATION OF DEG LACTIDE CAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare caprolactone/DEG lactide copolymers. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and DEG lactide monomer from Example 19. The polymers were discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLES 30 & 31

PREPARATION OF POLYETHYLENE GLYCOL CAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare caprolactone/PEG copolymers. The PEG used was determined by GPC to have an Mn of 4230. Alternatively, higher or lower molecular weight PEG's could be utilized in the synthesis of these copolymers. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and PEG 4000 monomer. The polymers were discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 32

PREPARATION OF EG/BDO ADIPATE MONOMER

Mixed diol adipates containing ethylene glycol (EG) and 1,4-butanediol (BDO) were prepared in a procedure substantially similar to that described in Example 12. The acid number and GPC molecular weight of the product were determined.

EXAMPLES 33 & 34

PREPARATION OF EG/BDO ADIPATE CAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare caprolactone/EG/BDO adipate copolymers. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and EG/BDO adipate monomer from Example 32. The polymers were discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 35
PREPARATION OF DEG/BDO ADIPATE MONOMER

Mixed diol adipates containing diethylene glycol (DEG) and 1,4-butanediol (BDO) were prepared in a procedure substantially similar to that described in Example 12. The acid number and GPC molecular weight of the product were determined.

EXAMPLE 36
PREPARATION OF DEG/BDO ADIPATE CAPROLACTONE COPOLYMER

A procedure substantially similar to that described in Example 1 was used to prepare caprolactone/DEG/BDO adipate copolymer. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and DEG/BDO adipate monomer from Example 35. The polymer was discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLE 37
PREPARATION OF DEG ADIPATE MONOMER

DEG adipate was prepared in a procedure substantially similar to that described in Example 6, except that the reaction was continued until the acid number was < 4. The acid number and GPC molecular weight of the product were determined.

EXAMPLES 38 & 39

PREPARATION OF DEG ADIPATE CAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare caprolactone/DEG adipate copolymers. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and DEG adipate monomer from Example 37. The polymers were discharged and converted into plaques for material testing, GPC, DSC, water swell.

EXAMPLES 40 & 41

PREPARATION OF SILOXANE CAPROLACTONE COPOLYMERS

A procedure substantially similar to that described in Example 1 was used to prepare caprolactone/polydimethylsiloxane copolymers. On a mole basis, the reactor was charged with the proper amount of ε-caprolactone monomer and hydroxy terminated polydimethylsiloxane, for example 40. The molecular weight of the polydimethylsiloxane can be in the range of 50 to 20000 g/gmole. For example 41, the reactor was charged with the proper amount of ε-caprolactone monomer and monohydroxy terminated polydimethylsiloxane.

EXAMPLE 42

BIODEGRADABILITY TEST

The biodegradability of a BEPD adipate initiated caprolactone copolymer from Example 10 was determined from the %Theoretical CO_2 produced using standard test method ASTM D-5338. A cellulose control was used and the samples were run in duplicate.

	Net Theoretical CO_2	
Days	Cellulose	BEPD ADIPATE Copolymer
1	1.46%	3.16%
3	25.37%	13.75%
5	50.03%	21.15%
10	70.04%	43.50%
15	77.15%	75.86%
20	84.00%	93.52%

EXAMPLE 43

GPC EVALUATION OF CAPROLACTONE POLYMERS

Example	2nd Monomer Type	2nd Monomer Mn	Polymer Mn	Polymer DI
1	DEG	106	139630	1.76
2	DEG	106	42640	1.96
3	DEG	106	33520	1.65
4	Penta	136	62320	1.40
5	Polybutadiene	3080	63990	2.22
7	BDO adipate	11990	81500	2.11
9	BEPD adipate	14120	101830	1.90
10	BEPD adipate	8820	77070	2.01
11	BEPD adipate +TMP	8820	95680	1.99
13	BEPD/EG adipate	8570	101460	2.14
14	NPG/BEPD adipate	12680	111040	2.25
15	NPG/BEPD adipate	12680	82740	2.30
17	BEPD adipate lactide	7390	86380	2.27
18	BEPD adipate lactide	7390	60150	2.27
20	DEG lactide	9460	85710	2.04
21	DEG lactide	10140	55050	1.84
22	DEG lactide	10140	51940	1.86
23	DEG lactide	10140	49860	1.93
24	DEG lactide	15390	53080	2.07
25	DEG lactide	15390	53570	2.04
26	DEG lactide	15390	49870	2.00
27	DEG lactide	15390	47630	2.00
28	DEG lactide	15390	48100	1.95
29	DEG lactide	15390	45150	1.93
30	PEG	4230	55680	1.60
31	PEG	4230	49590	1.54
33	EG/BDO adipate	5000	12340	2.79
34	EG/BDO adipate	10480	51670	2.34

EXAMPLE 43 (continued)

GPC EVALUATION OF CAPROLACTONE POLYMERS

Example	2nd Monomer Type	2nd Monomer Mn	Polymer Mn	Polymer DI
36	DEG/BDO adipate	6300	40140	2.24
38	DEG adipate	11690	89330	2.15
39	DEG adipate	11690	40290	2.05
40	PDMS, dihydroxy	3891	37830	2.10
41	PDMS, monohydroxy	1600	68980	2.27

EXAMPLE 44

DSC EVALUATION OF CAPROLACTONE POLYMERS

Examples 1-3 are control caprolactone polymers of various molecular weights for comparison purposes. Examples 4, 5, 7, 30 and 31 do not have reduced crystallinity. Examples 5, 7, 30, 31,40 and 41 are representative of copolymers that do not have reduced crystallinity with the introduction of semi-crystalline second monomers. Examples 11 and 13 have a slight decrease in crystallinity. Examples 9 and 10 reveal the effectiveness of higher second monomer Mn in decreasing the crystallization temperature, the melting temperature and the % crystallinity. Examples 10, 17, 18, 36 and 39 are representative of copolymers that have moderate reduction in crystallinity vs homopolymer caprolactone. Examples 9, 14, 15 and 38 copolymers have a great decrease in crystallinity as compared to caprolactone polymer of similar molecular weight. In Examples 20 through 29, 33 and 34, the introduction of semicrystalline second monomers has led to copolymers having a significant reduction in crystallinity as compared to caprolactone polymers of similar molecular weight.

Ex	2nd Mono-mer Type	2nd Mono-mer Mn	Polymer Mn	Cryst. Temp C	Melt Temp C	Heat of Fusion, cal/g
1	DEG	106	139630	28.5	56.3	15.7
2	DEG	106	42640	26.9	57.4	17.2
3	DEG	106	33520	31.2	57.4	18.1
4	Pentae ry-thritol	136	62320	25.6	55.8	16.6
5	Polybut a-diene	3080	63990	26.2	56.6	15.7
7	BDO adipate	11990	81500	24.7	54.6	17.0
9	BEPD adipate	14120	101830	3.2	47.7	10.6
10	BEPD adipate	8820	77070	20.8	54.4	13.9
11	BEPD adipate +TMP	8820	95680	25.7	54.5	13.4
13	BEPD/ EG adipate	8570	101460	23.6	54.2	13.6
14	NPG/B EPD adipate	12680	111040	19.3	53.6	11.8
15	NPG/B EPD adipate	12680	82740	13.8	53.2	12.3
17	BEPD adipate lactide	7390	86380	21.9	54.5	14.9
18	BEPD adipate lactide	7390	60150	22.3	54.3	13.6
20	DEG lactide	9460	85710	11.7	40.9	11.6
21	DEG lactide	10140	55050	-16.0	32.0	7.0
22	DEG lactide	10140	51940	-14.0	36.3	8.0

Ex	2nd Mono-mer Type	2nd Mono-mer Mn	Polymer Mn	Cryst. Temp C	Melt Temp C	Heat of Fusion, cal/g
23	DEG lactide	10140	49860	-12.8	36.2	7.8
24	DEG lactide	15390	53080	15.2	50.8	11.4
25	DEG lactide	15390	53570	12.5	49.6	10.5
26	DEG lactide	15390	49870	-5.9	44.3	7.7
27	DEG lactide	15390	47630	none	39.1	4.6
28	DEG lactide	15390	48100	-19.5	40.1	0.9
29	DEG lactide	15390	45150	none	45.6	6.5
30	PEG	4230	55680	31.5	56.4	17.2
31	PEG	4230	49590	27.1	55.6	15.6
33	EG/BDO adipate	5000	12340	11.3	41.6	13.2
34	EG/BDO adipate	10480	51670	9.6	41.0	13.4
36	DEG/BDO adipate	6300	40140	23.8	54.9	15.9
38	DEG adipate	11690	89330	19.0	51.5	13.8
39	DEG adipate	11690	40290	25.9	54.5	12.6
40	PDMS, dihydroxy	3891	37830	27.0	56.9	16.7
41	PDMS, mono-hydroxy	1600	68980	28.4	56.1	14.1

EXAMPLE 45
WATER SWELL OF CAPROLACTONE POLYMERS

Examples 1, 2 and 3 are control caprolactone polymers of various molecular weights for comparison purposes. Some of the polymers, although lower in crystallinity than the caprolactone polymers, did not absorb more water than the control samples. Lower molecular weight samples of examples 4 through 10 would result in a further decrease in crystallinity and would therefore be expected to have improved water uptake. Examples 21, 23, 25, 26, 27, and 28 had increased water swell and also had reduced crystallinity as shown in Example 44. Examples 30 and 31 show a great increase in water swell as compared to a homopolymer of caprolactone of similar molecular weight. This is believed to be due to the chemical structure of the second monomer, an ether. Examples 33 and 38 are indicative of samples with reduced crystallinity and improved water swell.

Ex.	2nd Monomer Type	2nd Monomer Mn	Polymer Mn	Water uptake, %
1	DEG	106	139630	0.51
2	DEG	106	42640	0.46
3	DEG	106	33520	0.44
4	Pentaerythritol	136	62320	0.25
5	Polybutadiene	3080	63990	0.32
7	BDO adipate	11990	81500	0.58
10	BEPD adipate	8820	77070	0.44
11	BEPD adipate +TMP	8820	95680	0.42
13	BEPD/EG adipate	8570	101460	0.49
15	NPG/BEPD adipate	12680	82740	0.41
18	BEPD adipate lactide	7390	60150	0.38
21	DEG lactide	10140	55050	1.37

Ex.	2nd Monomer Type	2nd Monomer Mn	Polymer Mn	Water uptake, %
23	DEG lactide	10140	49860	1.07
25	DEG lactide	15390	53570	0.54
26	DEG lactide	15390	49870	0.63
27	DEG lactide	15390	47630	0.97
28	DEG lactide	15390	48100	1.30
30	PEG	4230	55680	6.14
31	PEG	4230	49590	7.98
33	EG/BDO adipate	5000	12340	1.02
38	DEG adipate	11690	89330	0.67

EXAMPLE 46

VICAT SOFTENING TEMPERATURE OF CAPROLACTONE POLYMERS

Ex	2nd Monomer Type	2nd Monomer Mn	Polymer Mn	Melt Temp °C	Vicat Temp, °C
1	DEG	106	139630	56.3	55.9
2	DEG	106	42640	57.4	54.5
3	DEG	106	33520	57.4	55.9
4	Pentaery-thritol	136	62320	55.8	55.0
5	Polybutadiene	3080	63990	56.6	55.3
7	BDO adipate	11990	81500	54.6	53.2
9	BEPD adipate	14120	101830	47.7	45.5
10	BEPD adipate	8820	77070	54.4	52.4
11	BEPD adipate +TMP	8820	95680	54.5	51.2
13	BEPD/EG adipate	8570	101460	54.2	52.7
14	NPG/BEPD adipate	12680	111040	53.6	51.0
15	NPG/BEPD adipate	12680	82740	53.2	50.4
17	BEPD adipate lactide	7390	86380	54.5	53.0

Ex	2nd Monomer Type	2nd Monomer Mn	Polymer Mn	Melt Temp °C	Vicat Temp, °C
18	BEPD adipate lactide	7390	60150	54.3	53.1
20	DEG lactide	9460	85710	40.9	<23.0
21	DEG lactide	10140	55050	32.0	26.9
22	DEG lactide	10140	51940	36.3	<23.0
23	DEG lactide	10140	49860	36.2	27.8
24	DEG lactide	15390	53080	50.8	42.5
25	DEG lactide	15390	53570	49.6	42.4
26	DEG lactide	15390	49870	44.3	<23.0

EXAMPLE 46

VICAT SOFTENING TEMPERATURE OF CAPROLACTONE POLYMERS

Ex	2nd Monomer Type	2nd Monomer Mn	Polymer Mn	Melt Temp °C	Vicat Temp, °C
27	DEG lactide	15390	47630	39.1	<23.0
28	DEG lactide	15390	48100	40.1	<23.0
29	DEG lactide	15390	45150	45.6	<23.0
30	PEG	4230	55680	56.4	53.8
31	PEG	4230	49590	55.6	53.2
33	EG/BDO adipate	5000	12340	41.6	38.1
36	DEG/BDO adipate	6300	40140	54.9	52.8
38	DEG adipate	11690	89330	51.5	50.5
39	DEG adipate	11690	40290	54.5	50.6

EXAMPLE 47

IMPROVED POLYMER REMOVABILITY FROM SURFACES

As compared to a homopolymer of caprolactone, TONE P767, examples 9, 21, and 34 have reduced surface or wetting tension as compared to a homopolymer polycaprolactone sample. Examples 40 and 41 have a very significant reduction in wetting tension as well as

in coefficient of friction. Example 39 has a reduction in the static coefficient of friction. Examples 9 and 34 as well as 21 have higher coefficient of friction than a homopolymer caprolactone sample. This is believed to be due to the low melting and softening points of these polymers. Example 21 softened to the touch and could not be measured.

Ex	2nd Monomer Type	Initiator Mn	Polymer Mn	Wetting Tension, dyne/cm	COF (static)	COF (kinetic)
9	BEPD adipate	14120	101830	34	0.53	0.94
21	DEG Lactide	10140	55050	36	-	-
34	EG/BDO adipate	10480	51670	36	0.36	0.51
39	DEG Adipate	11690	40290	42	0.24	0.43
40	PDMS	3891	37830	<30	0.16	0.16
41	mono-hydroxy terminated PDMS	1600	68980	<30	0.23	0.23
P767	DEG	106	76850	42	0.31	0.40

EXAMPLE 48

PREPARATION OF GUM BASE

A gum base composition is prepared with the following ingredients:

INGREDIENTS	PERCENT BY WEIGHT
Copolymer of Example 9	20.00
Butyl Rubber[1]	2.00
Polyisobutylene[2]	6.00
Polyvinyl Acetate (MW = 12,800 g/gmol))	23.75
Polyvinyl Acetate (MW = 47,000)	31.50
Glycerol Triacetate	6.75
Calcium Carbonate	10.00

[1] Polyisobutylene-isoprene copolymer having a weight average molecular weight of 400,000 g/gmol.

[2] Polyisobutylene having a weight average molecular weight of 42,600 to 46,100 g/gmol.

The gum base is prepared as follows:

Butyl rubber is added to a mixing kettle that had been preheated for 1 hour to a temperature of about 115° to 120° C. using steam under a pressure of about 30 psig and then masticated for about 1 hour. The rubber is broken into small pieces and softened with steam heat and mechanical action on the kettle. One third portion of the

polyisobutylene is then added to the kettle and mixed for about 10 to 15 minutes until the mixture becomes homogeneous. Another one third portion of the polyisobutylene is then added to the kettle and mixed for 10 to 15 minutes until the mixture becomes homogeneous. The remaining one third portion is then added to the kettle and mixed for 30 to 45 minutes until the whole mixture becomes homogeneous and has a consistent texture. The mixture is then discharged into the pan and allowed to cool to room temperature.

The mixture is then added to the mixing kettle, which had again been preheated for 1 hour to a temperature of 110° to 120°C. using steam under a pressure of about 30 psig, and mixed for 10 to 15 minutes. Calcium carbonate is then added to the kettle and mixed for 10 to 15 minutes until a homogeneous mixture is obtained. Polyvinyl acetate having a molecular weight of 47,000 g/gmol and the copolymer of Example 7 are then added to the kettle and mixed for about 20 to 25 minutes until it is softened and blended into the homogeneous mixture. Polyvinyl acetate having a molecular weight of 12,800 g/gmol is then added to the kettle and mixed for 20 to 25 minutes until the mixture becomes smooth. The steam is then shut off. Glycerol triacetate is then slowly added to the kettle in 10 to 15 minutes. The homogeneous mixture is then discharged into the pan and allowed to cool to room temperature from the discharge temperature of 105° to 110°C. to obtain a gum base composition.

EXAMPLE 49
CHEWING GUM FORMULATION

A chewing gum formulation is prepared with the following ingredients:

INGREDIENTS	PERCENT BY WEIGHT
Gum Base from Example 48	26.000
Glycerol Triacetate	0.250
Lecithin	0.500
Crystalline Sorbitol	40.780
Mannitol	15.000
Glycerin	12.000
Peppermint Flavors	1.800
Aspartame	0.170
Encapsulated Aspartame	1.000
Amorphous Silica	1.000
Polyoxyethylene (20)	1.000
Sorbitan Monooleate Non-Hydrogenated Cotton Seed Oil	0.500

The gum base from Example 48 is melted at a temperature of 80° to 85°C. The molten gum base is then poured into a mixing kettle. Lecithin, polyoxyethylene (20) sorbitan monooleate, non-hydrogenated cotton seed oil, and glycerol triacetate are then added to the kettle and mixed for 1 to 2 minutes. 2/3 crystalline sorbitol, mannitol, and amorphous silica are then added to the kettle and mixed for 2 minutes. The mixture is held for 1 minute and then glycerin is added while mixing the mixture. The remaining 1/3 crystalline sorbitol is then added and mixed for 2 minutes. While mixing, the peppermint flavors are added. The aspartame sweeteners are then added and mixed for 3 minutes. The gum mixture is then discharged to a pan at temperature

of 43° to 46°C. The gum is then rolled and scored to the proper dimensions on a Rolling and Scoring Machine.

In addition to the specific aspects of the invention disclosed herein, those skilled in the art will recognize that other aspects are intended to be within the scope of the invention.

We Claim:

1. An improved, degradable gum base comprising at least one degradable polymer, characterized in that the degradable polymer is a copolymer polymerized from:

(a) about 51 to 99.9 wt % of a first monomer which is polymerizable by condensation polymerization, said percentage based on the total weight of the copolymer; and

(b) about 0.1 to 49 wt % of a second monomer which is copolymerizable with the first monomer, said percentage based on the total weight of the copolymer;

wherein the second monomer is effective to suppress the crystallinity of the copolymer.

2. The gum base in claim 1 wherein the copolymer is biodegradable.

3. The gum base of claim 1 wherein the first monomer has a functional group selected from the group consisting of esters, ethers, carbonates, acetals, alcohols, acids, amines, amides, acid halides, isocyanates and mixtures thereof.

4. The gum base of claim 1 wherein the first monomer is cyclic.

5. The gum base of claim 1 wherein the first monomer is selected from the group consisting of lactones, lactams, polyols, urethanes, ureas, carbonates, acetals, and mixtures thereof.

6. The gum base of claim 1 wherein the first monomer is selected from the group consisting of caprolactone and derivatives thereof.

7. The gum base of claim 1 wherein the second monomer is effective to initiate the polymerization of the first monomer.

8. The gum base of claim 1 wherein the second monomer has a functional group selected from the group consisting of esters, ethers, carbonates, acetals, alcohols, acids, amines, amides, acid halides, isocyanates and mixtures thereof.

9. The gum base of claim 1 wherein the second monomer is selected from the group consisting of adipate esters, lactides and lactones.

10. The gum base of claim 1 wherein the second monomer is effective to introduce amorphous regions in the copolymer.

11. The gum base of claim 1 wherein the second monomer is a prepolymer having a molecular weight of from about 500 to 25,000 g/gmole.

12. The gum base of claim 1 which is polymerized from about 80 to 99 weight percent of the first monomer and from about 1 to 20 weight percent of the second monomer.

13. The gum base of claim 1 wherein the copolymer has a melting temperature depression of at least about 2°C.

14. The gum base of claim 1 wherein the copolymer has a reduction in Vicat softening point of at least about 2°C.

15. The gum base of claim 1 wherein the water uptake of the copolymer is at least 5% greater than the water uptake of a homopolymer of the first monomer.

16. The gum base of claim 1 wherein the copolymer is effective to enhance the removability of the gum base.

17. The gum base of claim 1 further comprising an elastomer.

18. The gum base of claim 1 further comprising a synthetic thermoplastic polymer.

19. The gum base of claim 18 wherein the thermoplastic polymer is selected from the group consisting of polyvinyl acetate, polyvinyl alcohol, ethylene vinyl/acetate and mixtures thereof.

INTERNATIONAL SEARCH REPORT

Inter[illegible]plication No
PCT/US 00/35614

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A23G3/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, FSTA, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 057 537 A (SINCLAIR RICHARD G) 8 November 1977 (1977-11-08) column 10, line 31 - line 34; example VIII	1-16
X	EP 0 711 506 A (UNIV GRONINGEN) 15 May 1996 (1996-05-15) claims 1,6-9; examples 1-3 & US 5 672 367 A 30 September 1997 (1997-09-30) cited in the application	1-11, 13-16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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[redacted]formation on patent family members

Inter[redacted]plication No
PCT/US 00/35614

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4057537 A	08-11-1977	NONE	
EP 0711506 A	15-05-1996	NL 9401703 A	01-05-1996
		FI 954867 A	15-04-1996
		JP 8196214 A	06-08-1996
		US 5672367 A	30-09-1997